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APPLICATION FOR UNITED STATES LETTERS PATENT

S P E C I F I C A T I O N

TO ALL WHOM IT MAY CONCERN:

Be it known that we, Dong-su PARK, a citizen of Republic of
Korea, residing at 201 Yujin Villa, 410-7 Changjun-dong, Icheon-shi,
Gyeonggi-do, Republic of Korea, and Kwang-seok JEON, a citizen of Republic
of Korea, residing at 101 Royal Juteak, 411-8 Changjun-dong, Icheon-shi,
Gyeonggi-do, Republic of Korea, have invented a new and useful METHOD
FOR MANUFACTURING TANTALUM OXY NITRIDE CAPACITORS, of which
the following is a specification.

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**METHOD FOR MANUFACTURING
TANTALUM OXY NITRIDE CAPACITORS**

5

BACKGROUND

TECHNICAL FIELD

A method for manufacturing a capacitor with a
10 tantalum oxy nitride (TaON) film for a semiconductor
device is disclosed. More particularly, a method for
manufacturing a capacitor is disclosed with a reduced
number of steps and thus an increased yield by in-situ
performing the step of executing P-doping after forming a
15 MPS (Metastable Poly Silicon) on a lower electrode and
the step of forming a nitride film before forming a
tantalum oxy nitride film. The disclosed method prevents
the concentration of phosphor contained in the lower
electrode from being reduced by removing the phosphor on
20 the surface of the lower electrode in a cleaning process
performed between the above two steps, thereby increasing
the capacitance of the capacitor.

DESCRIPTION OF THE RELATED ART

25 Generally, a capacitor stores a charge required for
the operation of a semiconductor. As the semiconductor
device is highly integrated, the size of a cell decreases
while the capacitance required for the operation of the
device slightly increases. Presently, the capacitance
30 required for devices of more than 64M DRAM is more than
30fF per cell.

In this way, with the high integration of the
semiconductor device, the miniaturization of the

capacitor is also being required. However, there is a limit to the size needed for storing charge for satisfying a required capacitance. Thus, there occurs a difficulty in miniaturizing the capacitor.

5 In consideration of this difficulty, the structure for storing charge of the capacitor is changed in various ways. The method for increasing charge of the capacitor includes the method for using tantalum oxy nitride (TaON), BST, etc. with a large dielectric constant as
10 dielectric, the method for reducing the thickness of a dielectric material and the method for increasing the surface area of the capacitor.

 Among them, the conventional process for forming a capacitor by using tantalum oxy nitride with a large
15 dielectric constant will now be described.

 First, a lower electrode 100 is formed by using material selected from undoped silicon, low doping silicon or doped/undoped silicon capable of MPS growth (the step of forming a lower electrode), then wet etching
20 or dry etching is performed on the formed lower electrode, then MPS is formed by using gas containing a silicon source (the step of forming MPS), and then P-Doping is performed by using a mixture of gases containing P (the step of doping MPS).

25 Next, a cleaning process is performed by using HF, BOE, sulfuric acid, SC-1, etc. in order to remove a native oxide film, a nitride film is formed on the resulting material of the above process, and then Si of the lower electrode is reacted with N of the formed
30 nitride film 102, for thereby forming a Si-N bond of 5~20Å on the surface of the lower electrode (the step of preprocessing tantalum oxy nitride).

After performing a preprocessing of tantalum oxy
nitride, an amorphous thin film 104 is deposited by using
chemical vapor containing tantalum by means of a surface
chemical reaction occurring on a wafer resulting in a
5 forming of a tantalum oxy nitride thin film.

Then, by nitrating or nitrifying the surface of the
resultant material by plasma, structural defects such as
micro cracks and pin holes on an interface can be
reinforced and homogeneity can be improved. Afterwards,
10 by forming an upper electrode 106 by stacking a metal
layer, a capacitor using tantalum oxy nitride can be
formed.

In the conventional process for forming a capacitor,
preprocessing of tantalum oxy nitride is performed in the
15 condition that plasma is excited in order to increase the
effect of a Si-N bond. Due to the increase in
temperature caused by the plasma, a problem occurs in
that a tantalum oxy nitride film deposited by the low
pressure chemical vapor deposition (LPCVD) is deposited
20 non-uniformly in the wafer and thus it is difficult to
meet process requirements. Particularly, it is necessary
that the tantalum oxy nitride film be deposited at a low
temperature of below 450°C, so the problem caused by the
increase in temperature may become more serious.

25 In addition, in the cleaning process between the MPS
doping step and the nitride film processing step of the
process for preprocessing tantalum oxy nitride, the
concentration of phosphor contained in the lower
electrode may be reduced by removing highly doped
30 phosphor by the MPS doping, which may lead to depletion
and thus reduce the capacitance of the capacitor.

SUMMARY OF THE DISCLOSURE

Therefore, a method for manufacturing a tantalum oxy
nitride capacitor is disclosed which reduces a number of
steps and increases yield by performing the step of
5 doping a MPS (Metastable Poly Silicon) in the same
chamber in-situ with the forming of a nitride film before
the forming of a tantalum oxy nitride film. The
disclosed method prevents the concentration of phosphor
contained in the lower electrode from being reduced by
10 removing the phosphor on the surface of the lower
electrode in a cleaning process performed between the
above two steps, thereby increasing the capacitance of
the capacitor.

In an embodiment, a method for manufacturing a
15 tantalum oxy nitride capacitor comprises: forming a
lower electrode on the surface of a semiconductor
substrate by using undoped silicon, low doped silicon or
doped/undoped silicon; forming MPS (Metastable Poly
Silicon) by using gases each containing a silicon source
20 after performing wet etching or dry etching of the formed
lower electrode; performing MPS doping by using mixed gas
containing P; depositing a nitride film, in the same
chamber of the MPS doping process as a tantalum oxy
nitride preprocessing step; depositing a tantalum oxy
25 nitride thin film by using chemical vapor containing
tantalum on the nitride film; performing a tantalum oxy
nitride postprocessing by nitrating or nitrifying the
surface of the thin film after the above depositing
process; and forming an upper electrode by stacking a
30 metal layer on the upper portion of the above resultant
material.

Also, where previously an MPS growing chamber, an
MPS doping chamber, and a tantalum oxy nitride chamber

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were separately required, the above processes from the
MPS formation step to the tantalum oxy nitride thin film
depositing step can be performed in the same chamber or
system. The above four processes such as MPS formation,
5 the MPS doping, the nitride depositing and the tantalum
oxy nitride film depositing are performed in the same
system or chamber.

In a method for manufacturing a capacitor according
to the disclosure, since the MPS doping step and a
10 nitride film depositing step before the tantalum oxy
nitride film formation are performed in the same chamber,
a cleaning process for removing a native oxide is
unnecessary, thereby preventing the phenomenon decreasing
capacitance of the capacitor and a bridge between cells
15 caused by crushing of MPS particles.

In a method for manufacturing a capacitor according
to the disclosure, since the MPS doping step and a
nitride film depositing step before the tantalum oxy
nitride film formation are performed at the same chamber,
20 a problem where a tantalum oxy nitride film is deposited
non-uniformly due to the increase in temperature caused
by the excited plasma is avoided.

In a method for manufacturing a capacitor according
to the disclosure as above, the etching to the lower
25 electrode can be performed by using gas contained HF,
especially, the mixed gas such as hydrogen fluoride/water
(HF/H₂O), hydrogen fluoride/hydrogen peroxide (HF/H₂O₂),
buffered oxide etchant (BOE), hydrogen fluoride/acetic
acid/nitrogen dioxide (HF/CH₃COOH/NO₂) etc. and mixture
30 thereof.

In the MPS formation step, a gas containing a
silicon source can be selected from the group consisting
of SiH₄, Si₂H₆, SiH₂Cl₂, mixtures thereof and performed at

a pressure below about 5×10^{-4} torr below and a temperature below about 700°C (on the basis of temperature of wafer).

The MPS doping step can be performed under a pressure ranging from about 1×10^{-3} to about 500 torr and at a temperature ranging from about 500 to about 1000°C , the gas containing P can be used a mixed gas containing PH_3 and the mixed gas containing PH_3 can be selected from the group consisting of PH_3/N_2 , PH_3/H_2 , PH_3/SiH_4 and PH_3/Ar .

Also, preferably, the nitride depositing step is performed by using NH_3 gas and under a pressure ranging from about 0.1 to about 200 torr and at a temperature ranging from about 600 to about 850°C .

In the tantalum oxy nitride film depositing, a tantalum compound such as tantalum ethylate is supplied to an evaporator or evaporating tube through a flow rate controller such as a MFC (mass flow controller), and then a predetermined amount thereof is evaporated at a temperature ranging from about 150 to about 200°C for thereby obtaining a chemical vapor of tantalum components. The chemical vapor and reaction gas, i.e., excessive O_2 gas and NH_3 gas obtained by the above method, each are controlled to a flow rate ranging from about 10 to about 1000sccm, are supplied and then are surface-reacted in a LPCVD chamber at a temperature ranging from about 300 to about 600°C , for thereby obtaining an amorphous tantalum oxy nitride thin film.

Also, the tantalum oxy nitride postprocessing step can be performed by nitrating the surface under NH_3 (or N_2/H_2 , N_2O , O_2) atmosphere at a temperature ranging from about 200 to about 600°C by using plasma or nitrifying the same under N_2O (or O_2) atmosphere. By performing the

postprocessing step as above, structural defects such as a micro crack and a pin hole on an interface can be reinforced and homogeneity can be improved. Although the characteristic of the tantalum oxy nitride is improved by this method, a process is added and therefore this step can be omitted if the electrical characteristic needed to a product is obtained in the high temperature heat treatment of the next step. Particularly, after depositing an amorphous tantalum oxy nitride thin film, in case of using a RTP (rapid thermal process) or an electric furnace, crystallization can be induced by a process for nitrating or oxidizing the resultant material for a time period ranging from about 30 seconds to about 120 minutes at a temperature ranging from about 650 to about 950°C under a NH_3 (or N_2/H_2 , N_2O , O_2) atmosphere.

In addition, in a step for forming an upper electrode, the upper electrode is formed by depositing the metal selected from the group consisting of poly silicon (Poly Si), titanium nitride (TiN), tantalum nitride (TaN), tungsten (W), tungsten nitride (WN), tungsten silicide (Wsi), ruthenium (RU), ruthenium oxide (RuO_2), iridium (Ir), platinum (Pt), etc. individually or in a stacking structure.

BRIEF DESCRIPTION OF THE DRAWINGS

The above features and advantages of the disclosure will become more apparent from the following detailed description taken in conjunction with the accompanying drawings, wherein:

Figs. 1 through 5 illustrate the sequence of processes for manufacturing a tantalum oxy nitride capacitor, in which:

Fig. 1 illustrates a resultant material obtained after forming a lower electrode and forming MPS (not shown) on the upper portion thereof;

Fig. 2 illustrates a resultant material obtained after performing MPS doping on the resultant material of Fig. 1;

Fig. 3 illustrates a resultant material obtained after performing a step of depositing a nitride film as a step of preprocessing tantalum oxy nitride;

Fig. 4 illustrates a resultant material obtained after depositing a tantalum oxy nitride thin film on the upper portion of the resultant material of Fig. 3; and

Fig. 5 illustrates a tantalum oxy nitride capacitor completed by forming an upper electrode on the upper portion of the resultant material of Fig. 4.

DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED EMBODIMENT

A preferred embodiment will now be described with reference to the accompanying drawings. But it is understood that the disclosure is not to be limited to this embodiment.

Figs. 1 through 5 are views illustrating the sequence of processes for manufacturing a tantalum oxy nitride capacitor.

In the process according to the disclosure, as illustrated in Fig. 1, a lower electrode 100 is formed on the surface of a semiconductor substrate 10. At this time, the lower electrode is selected from undoped silicon, low doping silicon or doped/undoped silicon which are capable of MPS growth. At this time, a thin film used as the electrode is an amorphous silicon film deposited at a temperature of below about 560°C by using

a gas containing a silicon source such as SiH_4 , Si_2H_6 , SiH_2Cl_2 and the like and a gas containing PH_3 such as PH_3/N_2 , PH_3/He , PH_3/SiH_4 , PH_3/Ar and the like. At this time, conditions such as an amount of gas, pressure, etc.

5 can be made suitable for a selective polycrystalline silicon growing technique (MPS growing technique).

Next, the thusly formed lower electrode is wet/dry etched by using a mixture of gases such as $\text{HF}/\text{H}_2\text{O}$, $\text{HF}/\text{H}_2\text{O}_2$, BOE, $\text{HF}/\text{CH}_3\text{COOH}/\text{NO}_2$, etc., and it is stored in a
10 space keeping a constant pressure below about 1×10^{-2} torr while MPS is formed on the upper portion of the resultant material by using SiH_4 , Si_2H_6 and SiH_2Cl_2 each containing a silicon source under a pressure of below about 5×10^{-4} torr (the MPS formation step). But, the
15 formed MPS has no relation with the characteristics of the present invention, so it is not shown in the drawings.

After the above process, P-doping is performed by using gas such as PH_3/N_2 , PH_3/H_2 , PH_3/SiH_4 , PH_3/Ar each
20 containing PH_3 under a pressure ranging from about 1×10^{-3} to about 500 torr and at a temperature ranging from about 500 to about 1000°C (the MPS doping step). Fig. 2 is a view illustrating a lower electrode onto which MPS doping is performed.

25 Then, in the same chamber ("in-situ"), a nitride film 102 is formed by using NH_3 gas under a pressure ranging from about 0.1 to about 200 torr and at a temperature ranging from about 600 to about 850°C . By this, the NH_3 is reacted with Si of the lower electrode,
30 for thereby forming a silicon-nitrogen (Si-N) bond on the surface of the lower electrode to a thickness ranging from about 5 to about 20\AA as illustrated in Fig. 3 (the tantalum oxy nitride preprocessing step).

After performing the tantalum oxy nitride preprocessing step, a tantalum compound such as tantalum ethylate is supplied to an evaporator or evaporating tube through a flow rate controller such as a MFC (mass flow controller), and then a predetermined amount thereof is evaporated at a temperature ranging from about 150 to about 200°C for thereby obtaining a chemical vapor of tantalum components. The chemical vapor and reaction gas, i.e., excessive O₂ gas and NH₃ gas, each are controlled to a flow rate ranging from about 10 to about 1000 sccm, are supplied and then are surface-reacted in a LPCVD chamber at a temperature ranging from about 300 to about 600°C, for thereby obtaining an amorphous tantalum oxy nitride thin film 104 as illustrated in Fig. 4 (the tantalum oxy nitride thin film formation step).

Afterwards, by nitrating the surface under NH₃ (or N₂/H₂) atmosphere at a temperature ranging from about 200 to about 600°C by using plasma or nitrifying the same under N₂O (or O₂) atmosphere in in-situ or ex-situ, structural defects such as a micro cracks and pin holes on an interface can be reinforced and homogeneity can be improved. Particularly, after depositing an amorphous tantalum oxy nitride thin film, in case of using a RTP (rapid thermal process) or an electric furnace, crystallization can be induced by a process for nitrating or oxidizing the resultant material for a time period ranging from about 30 seconds to about 120 minutes at a temperature ranging from about 650 to about 950°C under NH₃ (or N₂/H₂, N₂O, O₂) atmosphere (the tantalum oxy nitride postprocessing step).

After performing the postprocessing step, as illustrated in Fig. 5, an upper electrode 106 is formed for thereby completing a capacitor according to the

present invention. As described above, the upper electrode can be formed by depositing poly silicon (Poly Si), titanium nitride (TiN), tantalum nitride (TaN), tungsten (W), tungsten nitride (WN), tungsten silicide (Wsi), ruthenium (RU), ruthenium oxide (RuO₂), iridium (Ir), platinum (Pt), etc. individually or in a stacking structure (the upper electrode formation step).

As seen from above, in the method for forming a tantalum oxy nitride capacitor, since the MPS doping step and the tantalum oxy nitride preprocessing step are performed in the same chamber (in-situ), depletion occurred due to the decrease in the concentration of P on the surface of the lower electrode caused by cleaning can be prevented. Thus, the capacitance of the capacitor can be increased, the crushing of MPS particles caused by cleaning can be prevented, and thus a bridge between cells by the MPS particles is blocked, for thereby reducing bit fail of the device.

In addition, the MPS formation step through the tantalum oxy nitride thin film formation step can be performed in-situ in the same system. Accordingly, equipment investment and process time can be reduced for thereby improving the productivity of the process.